## **DOXORUBICIN**

## **DAUNORUBICIN**

## FIG. 1. Structure of Doxorubicin and Daunorubicin

FIG. 2 Structure of WP831

FIG. 3 Structure of WP791

FIG. 4 Structure of WP790

FIG. 5 Structure of WP787

FIG. 6 Stucture of WP786

FIG. 7 Stucture of WP785

FIG. 8 Structure of WP784

FIG. 9 Structure of WP780

FIG. 10 Stucture of WP778

FIG. 11 Structure of WP775

FIG. 12 Structure of WP774

FIG. 13 Structure of WP758

FIG. 14 Structure of WP757

FIG. 15 Structure WP756

FIG. 16 Structure WP755

FIG. 17 Structure of WP799

FIG. 18 Structure of WP797

FIG. 19 Structure of WP794

WP783

FIG. 20 Structure of WP783

FIG. 21 Structure of WP750

FIG. 22 Structure of WP744

WP727

FIG. 23 Structure of WP727



FIG. 24 Structure of WP567

FIG. 25 Structure of WP793

FIG. 26 Structure of WP819

FIG. 27 Structure of WP820

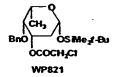


FIG. 28 WP821

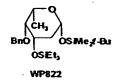


FIG. 29 Structure of WP822

FIG. 30 Structure of WP823

FIG. 31 Structure of WP824

FIG. 32 Structure of WP825

FIG. 33 Structure of WP764

FIG. 34 Structure of WP765

### SYNTHESIS OF 4'-O-BENZYLATED ANTHRACYCLINES FROM 4-O-BENZYLATED GLYCALS

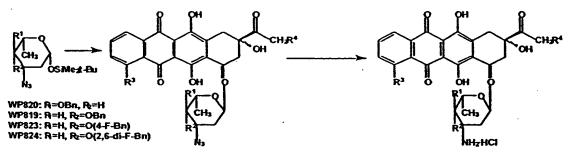
B. K<sub>2</sub>CO<sub>3</sub> THF, MeOH

C.Bu, NF, THF or H"

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### **FIG. 36**

#### SYNTHESIS OF 4'-O-BENZYL-3'-AMINO-ANTHRACYCLINES



WP783A: R=H, R=OBn, R=H, R=H WP797A: R=H, R=O(4-F)Bn, R=H, R=H WP750A: R=OBn, R=H, R=OMe, R=OSiPhd-Bu WP74AA: R=H, R=OBn, R=OMe, R=OSiMed-Bu WP799A: R=H, R=O(2,6-diF)Bn, R=OMe, R=OSiPhd-Bu WP769A: R=H, R=OBn, R=H, R=OSiPhd-Bu

WP783: R=H, R=OBn, R=H, R4=H WP797: R=H, R=O(4-F)Bn, R=H, R4=H WP750B: R=OBn, R4-H, R3=OMe, R3=OSiPh&Bu WP744B: R=H, R3=OBn, R3=OMe, R3=OSiMed-Bu WP799B: R=H, R3=O(2,6-diF)Bn, R3=OMe, R4=OSiPh&Bu WP769B: R=H, R3=OBn, R3=H, R4=OSiPh&Bu

OH

CHR4

OH

CHR4

WP750: R=OBn, R=H, R=OMe, R=OH

WP744: R=H, R=OBn, R=OMe, R=OH

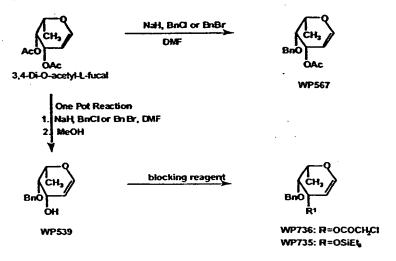
WP799: R=H, R=O(2,6-diF)Bn, R=OMe, R=OH

WP769: R=H, R=OBn, R=H, R=OH

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### FIG. 37

# SYNTHESIS OF 4-O-BENZYL-GLYCALS AND ITS 3-O-DERIVATIVES



The same procedure was used for the synthesis of otherO-benzylated glycals.

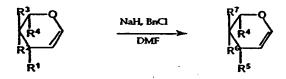
## SYNTHESIS OF 4'-O-BENZYL-3'-DEAMINO-ANTHRACYCLINES FROM 1-O-SILYLATED 4-O-BENZYL-HEXOPYRANOSES

WP793A: R ¹=OCOCH, CI, R¹=H, R²=H WP794A: R¹=OCOCH, CI, R²=H, R²=OSiPb, t-Bu WP571A: R¹=OSiEt, R¹=OMe, R¹=OCO(CH,), CI, WP568: R¹=OCOCH, R²=OMe, R³=OSiPb, t-Bu

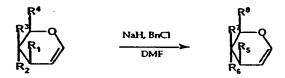
WP793: R <sup>3</sup>=H, R<sup>3</sup>=H WP794B: R<sup>2</sup>=H, R <sup>3</sup>= OSIPh,I-Bu WP571: R <sup>1</sup>=OMe, R <sup>3</sup>=OCO(CH<sub>3</sub>),CH<sub>3</sub> WP569: R <sup>3</sup>=OMe, R <sup>3</sup>=OSIPh,I-Bu

WP734: R<sup>2</sup>=H, R<sup>2</sup>=OH WP727: R<sup>2</sup>=OMe, R<sup>2</sup>=OH

### **Examples of Selective Alkylation of Acylated Glycals**



L-Rhamnal: WP- R  $^1$ =OAc, R $^2$ =H, R $^3$ =OAc, R $^4$ =Me, R $^5$ =OH, R $^6$ =H, R $^7$ =OBn L-Rhamnal: WP- R  $^1$ =OAc, R $^2$ =H, R $^3$ =OAc, R $^4$ =Me, R $^5$ =OAc, R $^6$ =H, R $^7$ =OBn L-Fucal: WP- R  $^1$ =OAc, R $^2$ =OAc, R $^3$ =H, R $^4$ =Me, R $^5$ =OH, R $^6$ =OBn, R $^7$ =H L-Yucal: WP- R  $^1$ =OAc, R $^2$ =OAc, R $^3$ =H, R $^4$ =Me, R $^5$ =OAc, R $^6$ =OBn, R $^7$ =H L-Xylal: WP- R  $^1$ =OAc, R $^2$ =H, R $^3$ =OAc, R $^4$ =H, R $^5$ =OAc, R $^6$ =H, R $^7$ =OBn

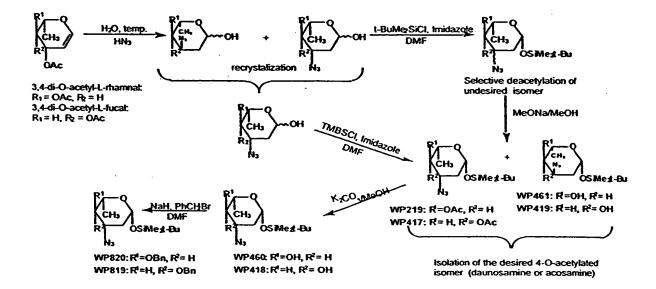


D-Glucal: WP-  $R^1$ =OAc,  $R^2$ =OAc,  $R^3$ =H,  $R^4$ =CH<sub>2</sub>OAc,  $R^5$ =OH,  $R^6$ =OBn,  $R^7$ =H,  $R^8$ =CH<sub>2</sub>OH D-Glucal: WP-  $R^1$ =OAc,  $R^2$ =OAc,  $R^3$ =H,  $R^4$ =CH<sub>2</sub>OAc,  $R^5$ =OAc,  $R^6$ =OBn,  $R^7$ =H,  $R^8$ =CH<sub>2</sub>OAc D-Galactal: WP-  $R^1$ =OAc,  $R^2$ =H,  $R^3$ =OAc,  $R^4$ =CH<sub>2</sub>OAc,  $R^5$ =OH,  $R^6$ =H,  $R^7$ =OBn,  $R^8$ =CH<sub>2</sub>OA D-Arabinal: WP-  $R^1$ =OAc,  $R^2$ =H,  $R^3$ =OAc,  $R^4$ =CH<sub>2</sub>OAc,  $R^5$ =Ac,  $R^6$ =H,  $R^7$ =OBn,  $R^8$ =CH<sub>2</sub>OA

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### FIG. 40

### Synthesis of 3'-azido-sugars and its 4-O-benzylated derivatives



#### ALTERNATIVE SYNTHESIS OF 3-AZIDO-4-O-BENZYL-DAUNOSAMINE FROM 3-AZIDOACOSAMINE

## FIG. 42 Structure of WP735



FIG. 43 Structure of WP736